



PCT/GB 2003 / 005664

REC'D	16 FEB 2004
WIPO	PCT



INVESTOR IN PEOPLE

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

**PRIORITY DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated 6 February 2004

**BEST AVAILABLE COPY**

24 DEC 2002

NEWPORT

27DEC02 E753486-3 C12133  
P01/7700 0.00-0230076.2**Request for grant of a patent**

*(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)*

The Patent Office

 Cardiff Road  
 Newport  
 South Wales  
 NP10 8QQ

1. Your reference

553

2. Patent application number

(The Patent Office will fill in this part)

0230076.2

24 DEC 2002

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)
 ELAM-T LIMITED  
 103 BOROUGH ROAD  
 LONDON  
 SE1 0AA

8105280001

Patents ADP number (*If you know it*)

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

ELECTROLUMINESCENT MATERIALS AND DEVICES

5. Name of your agent (*If you have one*)
 "Address for service" in the United Kingdom  
 to which all correspondence should be sent  
*(including the postcode)*

 COHEN, ALAN NICOL  
 2 GROVE PLACE  
 TATSFIELD  
 Nr. WESTERHAM  
 KENT  
 TN16 2BB

6963557001

Patents ADP number (*If you know it*)
 6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (*If you know it*) the or each application number

Country

Priority application number  
*(If you know it)*Date of filing  
*(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
*(day / month / year)*
 8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (*Answer 'Yes' if*)

YES

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

*See note (d)*

**Patents Form 1/77**

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form

Description 21

Claim(s) 6

Abstract 1

Drawing(s) 20 + 20

---

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination  
(*Patents Form 10/77*)

Any other documents  
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date 23/12/02

---

12. Name and daytime telephone number of person to contact in the United Kingdom

A. N. Cohen

01959 577172

**Warning**

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

**Notes**

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

### Electroluminescent Materials and Devices

The present invention relates to electroluminescent materials and to electroluminescent devices.

5 Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications. Liquid crystal devices and devices which are based on inorganic semiconductor systems are widely used, however these suffer from the disadvantages of high energy consumption, high cost of manufacture, low quantum efficiency and the inability to make flat panel displays.

10 Organic polymers have been proposed as useful in electroluminescent devices, but it is not possible to obtain pure colours, they are expensive to make and have a relatively low efficiency.

15 Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

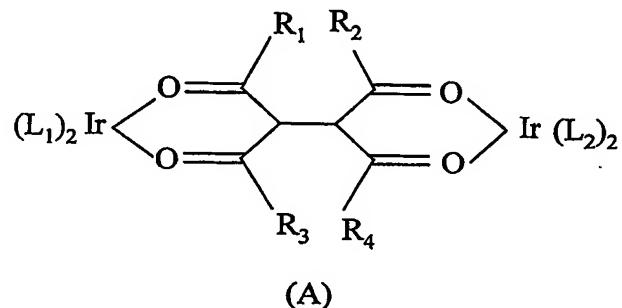
20 Patent application WO98/58037 describes a range of lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 describe electroluminescent complexes, structures and devices using rare earth chelates.

25 US Patent 5128587 discloses an electroluminescent device which consists of an organometallic complex of rare earth elements of the lanthanide series sandwiched between a transparent electrode of high work function and a second electrode of low work function with a hole conducting layer interposed between the electroluminescent layer and the transparent high work function electrode and an

electron conducting layer interposed between the electroluminescent layer and the electron injecting low work function anode. The hole conducting layer and the electron conducting layer are required to improve the working and the efficiency of the device. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

We have now devised electroluminescent compounds and electroluminescent structures incorporating them.

According to the invention there is provided an electroluminescent diiridium compound of formula



where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures,

- 3 -

fluorine, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups or nitrile and L<sub>1</sub> and L<sub>2</sub> are the same or different organic ligands.

Examples of R<sub>1</sub> and/or R<sub>2</sub> and/or R<sub>3</sub> and/or R<sub>4</sub> include aliphatic, aromatic and  
5 heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl,  
fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl  
groups such as t-butyl, heterocyclic groups such as carbazole.

Preferred organic ligands L<sub>1</sub> and L<sub>2</sub> are phenyl pyridine and substituted  
10 phenylpyridines.

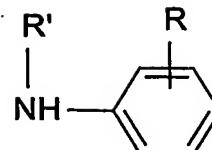
The invention also provides an electroluminescent device which comprises (i) a first electrode (ii) a layer of the diiridium complex (A) and (iii) a second electrode.

15 The first electrode can function as the cathode and the second electrode can function as the anode and preferably there is a layer of a hole transporting material between the anode and the layer of the electroluminescent compound.

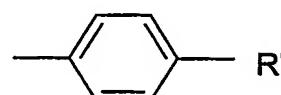
20 The hole transporting material can be any of the hole transporting materials used in electroluminescent devices.

25 The hole transporting material can be an amine complex such as poly (vinylcarbazole), N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), an unsubstituted or substituted polymer of an amino substituted aromatic compound, a polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes etc. Examples of polyanilines are polymers of

- 4 -



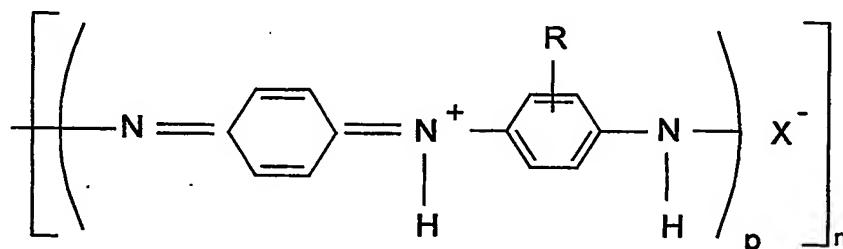
where R is in the ortho - or meta-position and is hydrogen, C1-18 alkyl, C1-6 alkoxy, amino, chloro, bromo, hydroxy or the group



5

where R is alkyl or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula I above.

10 Or the hole transporting material can be a polyaniline, polyanilines which can be used in the present invention have the general formula



XXVII

15 where p is from 1 to 10 and n is from 1 to 20, R is as defined above and X is an anion, preferably selected from Cl, Br, SO<sub>4</sub>, BF<sub>4</sub>, PF<sub>6</sub>, H<sub>2</sub>PO<sub>3</sub>, H<sub>2</sub>PO<sub>4</sub>, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate alkysulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulose sulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

20 Examples of arylsulphonates are p-toluenesulphonate, benzenesulphonate, 9,10-anthraquinone-sulphonate and anthracenesulphonate, an example of an arenedicarboxylate is phthalate and an example of arenecarboxylate is benzoate.

We have found that protonated polymers of the unsubstituted or substituted polymer of an amino substituted aromatic compound such as a polyaniline are difficult to evaporate or cannot be evaporated, however we have surprisingly found that if the 5 unsubstituted or substituted polymer of an amino substituted aromatic compound is deprotonated the it can be easily evaporated i.e. the polymer is evaporable.

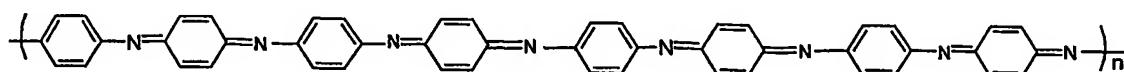
Preferably evaporable deprotonated polymers of unsubstituted or substituted polymer of an amino substituted aromatic compound are used. The de-protonated 10 unsubstituted or substituted polymer of an amino substituted aromatic compound can be formed by deprotonating the polymer by treatment with an alkali such as ammonium hydroxide or an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

15 The degree of protonation can be controlled by forming a protonated polyaniline and de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P319 1989.

20 The conductivity of the polyaniline is dependant on the degree of protonation with the maximum conductivity being when the degree of protonation is between 40 and 60% e.g. about 50% for example.

Preferably the polymer is substantially fully deprotonated

25 A polyaniline can be formed of octamer units i.e. p is four e.g.



The polyanilines can have conductivities of the order of  $1 \times 10^{-1}$  Siemen cm<sup>-1</sup> or higher.

The aromatic rings can be unsubstituted or substituted e.g. by a C1 to 20 alkyl group such as ethyl.

5 The polyaniline can be a copolymer of aniline and preferred copolymers are the copolymers of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with amino anthracenes.

10 Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonaphthalenes, polyaminoanthracenes, polyaminophenanthrenes, etc. and polymers of any other condensed polyaromatic compound. Polyaminoanthracenes and methods of making them are disclosed in US Patent 6,153,726. The aromatic rings can be unsubstituted or substituted e.g. by a

15 group R as defined above.

Other hole transporting materials are conjugated polymer and the conjugated polymers which can be used can be any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

20 The preferred conjugated polymers are poly (p-phenylenevinylene)-PPV and copolymers including PPV. Other preferred polymers are poly(2,5 dialkoxyphenylene vinylene) such as poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-  
25 dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

In PPV the phenylene ring may optionally carry one or more substituents e.g. each independently selected from alkyl, preferably methyl, alkoxy, preferably methoxy or ethoxy.

- 5 Any poly(arylenevinylene) including substituted derivatives thereof can be used and the phenylene ring in poly(p-phenylenevinylene) may be replaced by a fused ring system such as anthracene or naphthlyene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased e.g. up to 7 or higher.
- 10 The conjugated polymers can be made by the methods disclosed in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

The thickness of the hole transporting layer is preferably 20nm to 200nm.

- 15 The polymers of an amino substituted aromatic compound such as polyanilines referred to above can also be used as buffer layers with or in conjunction with other hole transporting materials.
- 20 The structural formulae of some other hole transporting materials are shown in Figures 12 to 16 of the drawings, where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R<sub>1</sub>,
- 25 R<sub>2</sub> and R<sub>3</sub> can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.
- 30

Examples of R<sub>1</sub> and/or R<sub>2</sub> and/or R<sub>3</sub> include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

5

In an embodiment of the invention the hole transporting material is mixed with the electroluminescent compound in the electroluminescent layer and a preferred electroluminescent compound is CBP which has the formula of fig. 4b the drawings.

10

There can be a buffer layer between the anode and the hole transporting layer and any of the hole transporting materials listed above can be used.

15

Optionally there is a layer of an electron injecting material between the cathode and the electroluminescent material layer, the electron injecting material is a material which will transport electrons when an electric current is passed through electron injecting materials include a metal complex such as a metal quinolate e.g. an aluminium quinolate, lithium quinolate, Mx(DBM)<sub>n</sub> where Mx is a metal and DBM is dibenzoyl methane and n is the valency of Mx e.g Mx is chromium. The electron injecting material can also be a cyano anthracene such as 9,10 dicyano anthracene, cyano substituted aromatic compounds, tetracyanoquinodimethane a polystyrene sulphonate or a compound with the structural formulae shown in figures 9 or 10 of the drawings in which the phenyl rings can be substituted with substituents R as defined above. Instead of being a separate layer the electron injecting material can be mixed with the electroluminescent material and co-deposited with it.

20

25 Optionally the hole transporting material can be mixed with the electroluminescent material and co-deposited with it.

The hole transporting materials, the electroluminescent material and the electron injecting materials can be mixed together to form one layer, which simplifies the construction.

5      The anode is preferably a transparent substrate such as a conductive glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer such as a metal or conductive polymer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the  
10     substrate.

15     The cathode is preferably a low work function metal e.g. aluminium, calcium, lithium, magnesium and alloys thereof such as silver/magnesium alloys, rare earth metal alloys etc., aluminium is a preferred metal. A metal fluoride such as an alkali metal, rare earth metal or their alloys can be used as the second electrode for example by having a metal fluoride layer formed on a metal.

20     The diiridium compound (A) can be mixed with other electroluminescent compounds for example europium complexes and the invention also provides an electroluminescent device which comprises (i) a first electrode (ii) a layer of an electroluminescent europium organo metallic or organic complex mixed with an iridium organo metallic or organic complex and (iii) a second electrode.

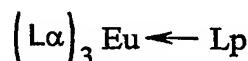
25     There is preferably also a layer of an electroluminescent europium organo metallic or organic complex and the invention also provides electroluminescent devices of structures:-

(i) a first electrode (ii) a layer of an electroluminescent europium organo metallic or organic complex (iii) a layer of an electroluminescent europium organo metallic or organic complex mixed with diiridium compound and (iv) a second electrode;

- 10 -

The electroluminescent europium organo metallic or organic complex preferably has the formula  $(L\alpha)_3Eu$  where  $L\alpha$  is an organic complex.

Preferred electroluminescent compounds which can be used in the present invention  
5 are of formula



(A)

where  $L\alpha$  and  $Lp$  are organic ligands and  $Lp$  is a neutral ligand. The ligands  $L\alpha$  can  
10 be the same or different and there can be a plurality of ligands  $Lp$  which can be the same or different.

For example  $(L_1)(L_2)(L_3)Eu$  ( $Lp$ ) where  $(L_1)(L_2)(L_3)$  are the same or different  
15 organic complexes and  $(Lp)$  is a neutral ligand and the different groups  $(L_1)(L_2)(L_3)$  may be the same or different

$Lp$  can be monodentate, bidentate or polydentate and there can be one or more ligands  $Lp$ .

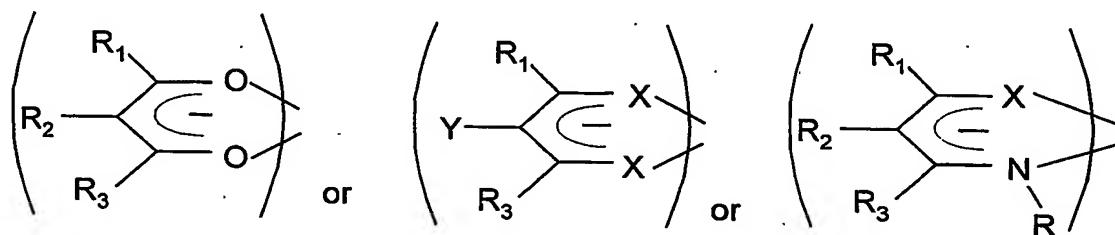
20 Further electroluminescent compounds which can be used in the present invention are of general formula  $(L\alpha)_nEuM_2$  where  $M_2$  is a non rare earth metal,  $L\alpha$  is as above and  $n$  is the combined valence state of  $Eu$  and  $M_2$ . The complex can also comprise one or more neutral ligands  $Lp$  so the complex has the general formula  $(L\alpha)_n Eu M_2$  ( $Lp$ ), where  $Lp$  is as above. The metal  $M_2$  can be any metal which is not a rare earth,  
25 transition metal, lanthanide or an actinide examples of metals which can be used include lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of

- 11 -

transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

5

Preferably  $L\alpha$  is selected from  $\beta$  diketones such as those of formulae



10

(I)

(II)

(III)

where  $R_1$ ,  $R_2$  and  $R_3$  can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups;  $R_1$ ,  $R_2$  and  $R_3$  can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene.  $X$  is Se, S or O,  $Y$  can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

15

20

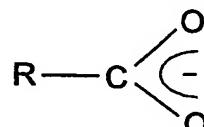
Examples of  $R_1$  and/or  $R_2$  and/or  $R_3$  include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

25

- 12 -

Some of the different groups  $L\alpha$  may also be the same or different charged groups such as carboxylate groups so that the group  $L_1$  can be as defined above and the groups  $L_2, L_3\dots$  can be charged groups such as

5



(IV)

where R is  $R_1$  as defined above or the groups  $L_1, L_2$  can be as defined above and  $L_3\dots$  etc. are other charged groups.

10  $R_1, R_2$  and  $R_3$  can also be



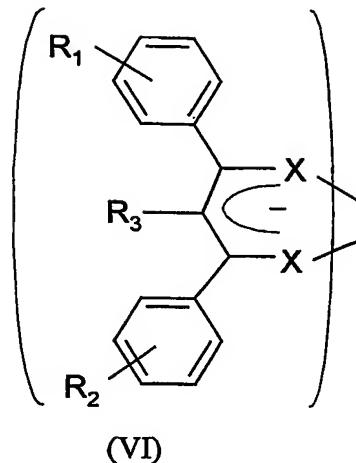
where X is O, S, Se or NH.

(V)

A preferred moiety  $R_1$  is trifluoromethyl  $CF_3$  and examples of such diketones are, banzoyltrifluoroacetone, p-chlorobenzoyltrifluoroacetone, p-bromotrifluoroacetone, 15 p-phenyltrifluoroacetone, 1-naphthoyltrifluoroacetone, 2-naphthoyltrifluoroacetone, 2-phenathoyltrifluoroacetone, 3-phenanthroyltrifluoroacetone, 9-anthroyltrifluoroacetone, cinnamoyltrifluoroacetone, and 2-thenoyltrifluoroacetone.

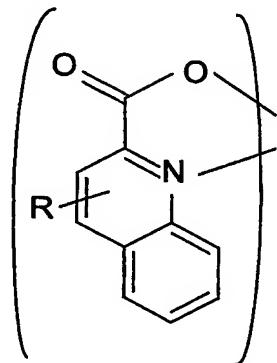
20 The different groups  $L\alpha$  may be the same or different ligands of formulae

- 13 -

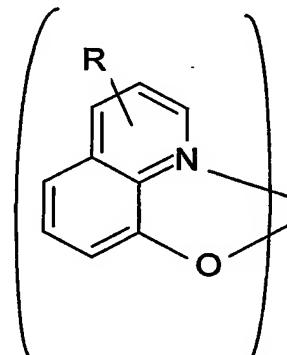


where X is O, S, or Se and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are as above

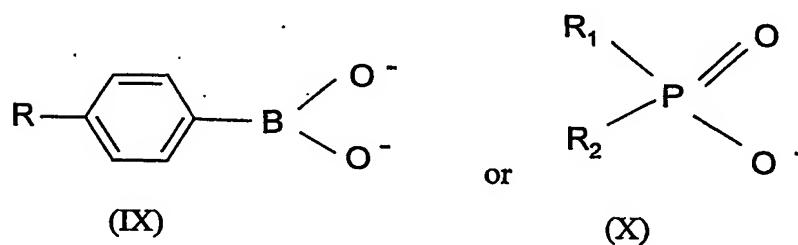
5. The different groups L<sub>α</sub> may be the same or different quinolate derivatives such as



or

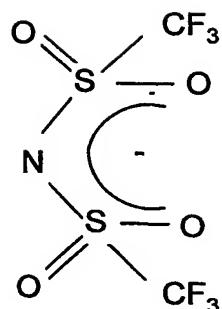


where R is hydrocarbyl, aliphatic, aromatic or heterocyclic carboxy, aryloxy, hydroxy or alkoxy e.g. the 8 hydroxy quinolate derivatives or



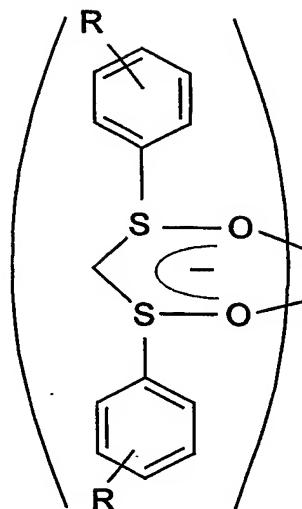
where R, R<sub>1</sub>, and R<sub>2</sub> are as above or are H or F e.g. R<sub>1</sub> and R<sub>2</sub> are alkyl or alkoxy groups

- 14 -



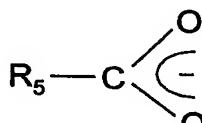
(XI)

or



(XII)

As stated above the different groups  $\text{L}\alpha$  may also be the same or different carboxylate groups e.g.

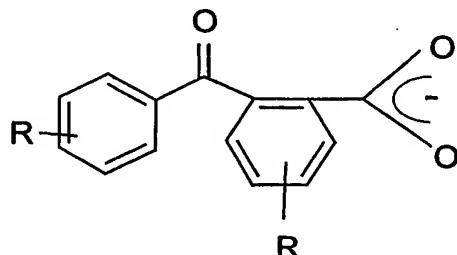


5

(XIII)

where  $\text{R}_5$  is a substituted or unsubstituted aromatic, polycyclic or heterocyclic ring a polypyridyl group,  $\text{R}_5$  can also be a 2-ethyl hexyl group so  $\text{L}_n$  is 2-ethylhexanoate or  $\text{R}_5$  can be a chair structure so that  $\text{L}_n$  is 2-acetyl cyclohexanoate or  $\text{L}\alpha$  can be

10



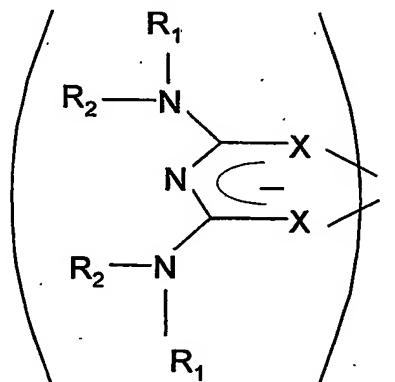
(XIV)

- 15 -

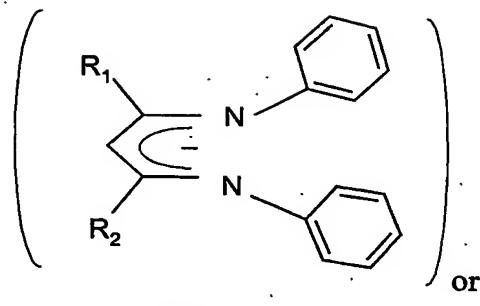
where R is as above e.g. alkyl, allenyl, amino or a fused ring such as a cyclic or polycyclic ring.

The different groups L $\alpha$  may also be

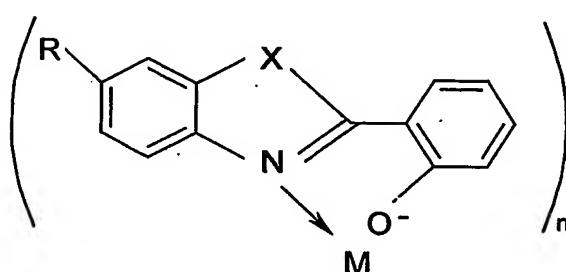
5



or

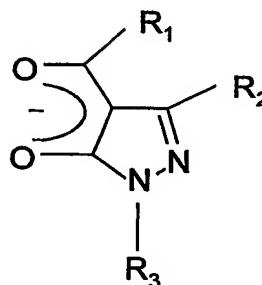


or



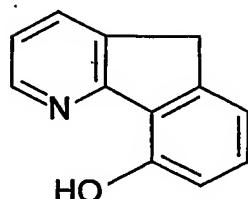
where X is O, S or Se

10

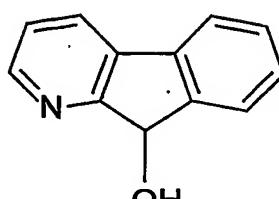


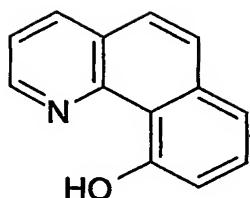
or

Where R, R<sub>1</sub> and R<sub>2</sub> are as above or



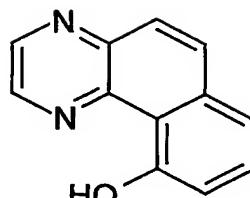
or





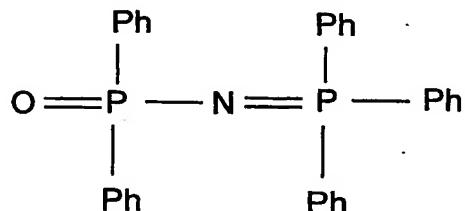
or

(XVIIId)



(XVIIle)

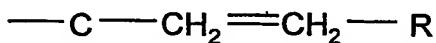
5 The groups  $L_P$  in the formula (A) above can be selected from



(XVIII)

Where each Ph which can be the same or different and can be a phenyl (OPNP) or a  
10 substituted phenyl group, other substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic or polycyclic group, a substituted or unsubstituted fused aromatic group such as a naphthyl, anthracene, phenanthrene or pyrene group. The substituents can be for example an alkyl, aralkyl, alkoxy, aromatic, heterocyclic, polycyclic group, halogen such as fluorine, cyano, amino.  
15 Substituted amino etc. Examples are given in figs. 1 and 2 of the drawings where R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be the same or different and are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can also be unsaturated alkylene groups such as vinyl groups or groups

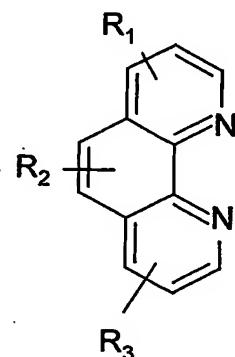
20



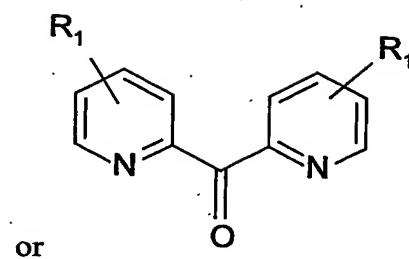
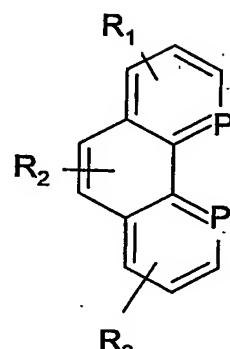
- 17 -

where R is as above.

$L_p$  can also be compounds of formulae



or



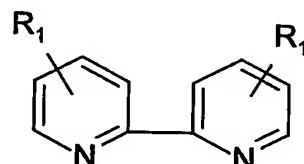
5

(XIV)

(XX)

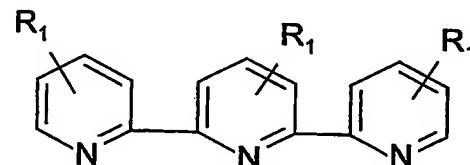
(XXI)

where  $R_1$ ,  $R_2$  and  $R_3$  are as referred to above, for example bathophen shown in fig. 3 of the drawings in which R is as above or



10

(XXII)

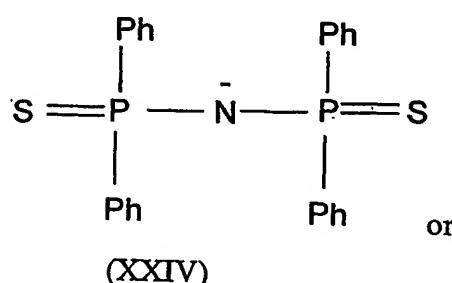


(XXIII)

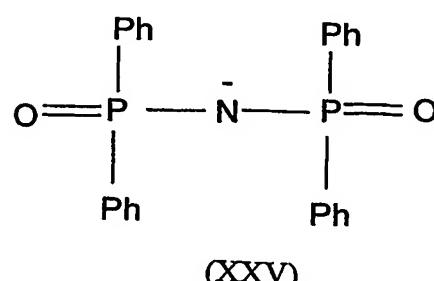
where  $R_1$ ,  $R_2$  and  $R_3$  are as referred to above.

$L_p$  can also be

15



or



(XXIV)

(XXV)

where Ph is as above.

Other examples of  $L_p$  chelates are as shown in figs. 4 and fluorene and fluorene derivatives e.g. a shown in figs. 5 and compounds of formulae as shown as shown in figs. 6 to 8.

5

Specific examples of  $L_\alpha$  and  $L_p$  are tripyridyl and TMHD, and TMHD complexes,  $\alpha, \alpha', \alpha''$  tripyridyl, crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA. Where TMHD is 2,2,6,6-tetramethyl-3,5-heptanedionato and OPNP is diphenylphosphonimide triphenyl phosphorane. The formulae of the polyamines are shown in fig. 11.

A preferred europium complex is  $\text{Eu(DBM)}_3\text{OPNP}$ .

A structure comprises (i) a first electrode (ii) a layer of a hole transporting (iii) a layer of an electroluminescent europium organo metallic or organic complex mixed with an iridium organo metallic or organic complex (iv) an electron transmitting layer and (v) a second electrode and preferably there is also one or more layers of a europium electroluminescent organo metallic or organic complex adjacent the layer (iii).

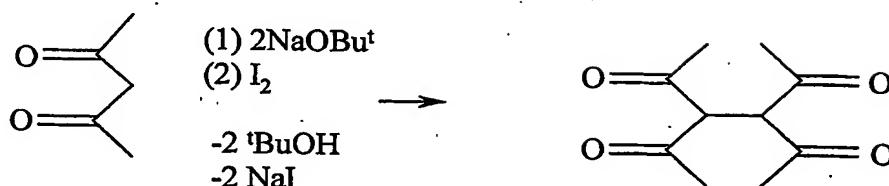
15 20 Optionally there can be other layers such as buffer layers e. in order that the holes and electrons combine in the electroluminescent layer and to improve the overall performance of the device.

25 The invention is illustrated in the examples in which exemplify the synthesis of the diridium complex.

30

- 19 -

Example 1 - 3,4-diacetyl-2,5-hexanedione (I)



5

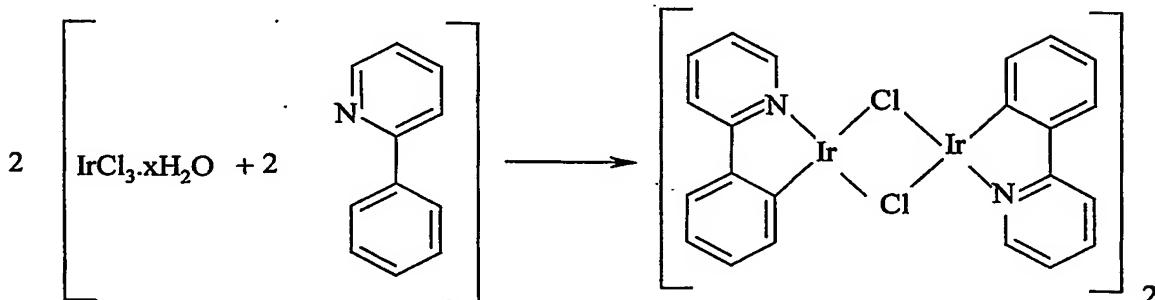
A three-necked 1 litre round-bottomed flask under an inert atmosphere (nitrogen) was charged with sodium tert-butoxide (30.0g, 310mmol) and a magnetic stirrer-bar. The .....(dried and distilled over Na/benzophenone, 500mL) was introduced, the temperature reduced to -78°C and pentane-2,4-dione (30.0g, 300mmol) in the 10 (dried and distilled over Na/benzophenone, 100mL) added over 30 mm. The reaction was allowed to warm to around 0°C and cooled with an ice-bath to maintain the temperature below 5°C. Iodine (38.0g, 150mmol) in the (dried and distilled over Na/benzophenone, 100mL) was added dropwise. The reaction mixture was stirred for 15 a further 30 mm with the ice-bath and then for 1 hour once the ice-bath had been removed. Diethylether (300mL) was added to the reaction mixture, which was then poured into 200mL saturated ammonium chloride solution (the pH was measured to ensure that the product had been neutralised). The organic layer was washed with 0.25M sodium thiosulfate solution (2 x 200mL) and then brine (200mL). The volatiles were removed *in vacuo* and the product recrystallised from ethanol (95%) to 20 yield colourless crystals (19.3g, 65%). M.p. 193-4°C. The product was used without further purification.

25

- 20 -

Example 2 -Tetrakis(2-phenylpyridine-C<sup>2</sup>, N')( $\mu$ -chloro) diiridium (II)

5



10 Iridium trichloride hydrate (0.388g) was combined with 2-phenylpyridine (0.76g), dissolved in a mixture of 2-ethoxyethanol (30mL, dried and distilled over MgSO<sub>4</sub>) and water (10mL), and refluxed for 24 hours. The solution was cooled to room temperature and the yellow/green precipitate collected on a glass sinter. The precipitate was washed with ethanol (60mL, 95%), acetone (60mL), and then dissolved in dichloromethane (75mL) and filtered. Toluene (25mL) and hexanes (10mL) were added to the filtrate and the volume reduced *in vacuo* to about 50mL. Cooling yielded crystals (yellow/green) of the desired product (0.43g, 72%). This was used without further purification.

15

20 Example 3 - Tetrakis(2-phenylpyridine-C<sup>2</sup>, N')( $\mu$ -3,4-diacetyl-2,5-hexanedionate) diiridium



25

Tetrakis(2-phenylpyridine-C<sup>2</sup>,N')( $\mu$ -chloro) diiridium (II) (0.5g, 0.47mmol), 3,4-diacetyl-2,5-hexanedione (I) (0.092g, 0.47mmol) and sodium carbonate (dried at 100°C, 200mg, 1.9mmol) were refluxed under an inert atmosphere (nitrogen) in 2-ethoxyethanol (dried and distilled over magnesium sulfate, 50mL) for 12 hours. On 5 cooling to room temperature, a yellow precipitate was collected on a sinter (porosity 3) and washed with water (50mL), hexane (50mL) and diethylether (50mL). The crude product was flash chromatographed on a silica column using dichloromethane as eluent. The dichloromethane was reduced in volume to about 5mL and then methanol (100mL) was added. The solution was, once more, reduced in volume to 10 about 50mL and the yellow product filtered (sinter, porosity 3) and washed with further methanol (100mL). The product was dried in a vacuum oven at 80°C for 2 hours. Yield (0.30g, 46%).

Device construction

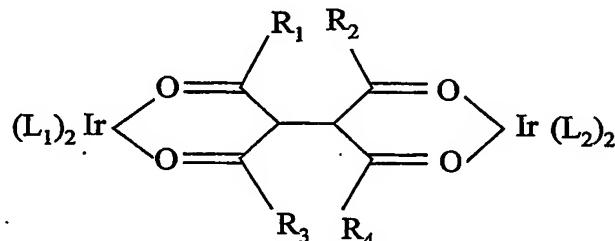
15 An electroluminescent device shown in fig. 17a was formed by a process in which an (indium tin oxide) ITO coated glass piece ( $1 \times 1\text{cm}^2$ ) had a portion etched out with concentrated hydrochloric acid to remove the ITO and was cleaned and dried. The device was fabricated by sequentially forming on the ITO, by vacuum evaporation at  $1 \times 10^{-5}$  Torr,, layers 1 to 7 where (1) is ITO, (2) is CuPc (3) is  $\alpha$ -NPB (4) is the 20 electroluminescent mixture (5) is BCP (6) is Alq<sub>3</sub> (7) is LiF and (8) isAl to form :-  
ITO/CuPc(8nm)/ $\alpha$ -NPB(40nm)/CBP+Ir<sub>2</sub>(diacac)<sub>2</sub> (dpp)<sub>2</sub> (12%)(20nm)/BCP(6nm)/Alq<sub>3</sub>(20nm)/LiF(0.7mn)Al  
Where CBP is shown in fig. 4b with R being H, BCP is bathocupron and Ir<sub>2</sub>(diacac)<sub>2</sub> (dpp)<sub>2</sub> is as synthesised in example 3.

25 An electric current was passed through the device and the properties of the emitted light measured and the results are shown in figs.18 to 20 of the drawings .

Claims

1. An electroluminescent diiridium compound of formula

5



where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile and L<sub>1</sub> and L<sub>2</sub> are the same or different organic ligands.

10

2. A diiridium compound as claimed in claim 1 in which L<sub>1</sub> and L<sub>2</sub> are phenyl pyridine and substituted phenylpyridines.

15

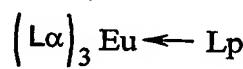
3. An electroluminescent device which comprises (i) a first electrode (ii) a layer of the diiridium complex as claimed in claim 1 or 2 and (iii) a second electrode.

- 23 -

4. An electroluminescent device as claimed in claim 3 in which the diirdium compound is mixed with an electroluminescent europium complex.

5. An electroluminescent device as claimed in claim 4 in which the europium organo metallic or organic complex has the formula  $(L\alpha)_3Eu$  where  $L\alpha$  is an organic complex.

6. An electroluminescent device as claimed in claim in which the europium organo metallic or organic complex has the formula



10

where  $L\alpha$  and  $Lp$  are organic ligands and  $Lp$  is a neutral ligand, the ligands  $L\alpha$  can be the same or different and there can be a plurality of ligands  $Lp$  which can be the same or different.

15

7. An electroluminescent device as claimed in claim 4 in which the europium organo metallic or organic complex has the formula  $(L\alpha)_nEuM_2$  where  $M_2$  is a non rare earth metal,  $L\alpha$  is as above and  $n$  is the combined valence state of Eu and  $M_2$ .

20

8. An electroluminescent device as claimed in claim 4 in which the europium organo metallic or organic complex has the formula formula  $(L\alpha)_n Eu M_2 (Lp)$ , where  $Lp$  is as above.

25

9. An electroluminescent device as claimed in claim 8 in which the metal  $M_2$  can be any metal which is not a rare earth, transition metal, lanthanide or an actinide.

10. An electroluminescent device as claimed in claim 8 in which the metal  $M_2$  is selected from lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium,

boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, 5 chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

11. An electroluminescent device as claimed in any one of claims 4 -10 in which  $L\alpha$  is of formula (I) to (XVII) herein.

10

12. An electroluminescent device as claimed in any one of claims 4 to 10 in which  $L_p$  is of formula (XVIII) to (XXV) herein or figs. 1 to 9 of the drawings

15

13. An electroluminescent device as claimed in any one of claims 4 to 12 in which  $L\alpha$  is selected from tripyridyl and TMHD, and TMHD complexes,  $\alpha$ ,  $\alpha'$ ,  $\alpha''$  tripyridyl and  $L_p$  is selected from crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA.

20

14. An electroluminescent device as claimed in any one of claims 4 to 13 in which the europium complex is  $Eu(DBM)_3OPNP$ .

15. An electroluminescent device as claimed any one of claims 3 to 14 in which there is a layer of a hole transmitting material between the first electrode and the electroluminescent layer.

25

17. An electroluminescent device as claimed in any one of claims 3 to 15 in which the hole transmitting material is polyaromatic amine complex.
18. An electroluminescent device as claimed in any one of claims 3 to 15 in which the hole transmitting material is a film of a polymer selected from poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl - 4,4'-diamine (TPD), polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes and substituted polysilanes.
19. An electroluminescent device as claimed in any one of claims 3 to 15 in which the hole transmitting material is a film of a compound of formula (XXVI) or (XXVII) herein or as in figures 4 to 8 of the drawings.
20. An electroluminescent device as claimed in any one of claims 3 to 15 in which the hole transmitting material is a copolymer of aniline, a copolymer of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with an amino anthracene.
21. An electroluminescent device as claimed in any one of claims 3 to 15 in which the hole transmitting material is a conjugated polymer.
22. An electroluminescent device as claimed in claim 21 in which the conjugated polymer is selected from poly (p-phenylenevinylene)-PPV and copolymers including PPV, poly(2,5 dialkoxyphenylene vinylene), poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, polythiophenes and oligothiophenes.

23. An electroluminescent device as claimed in any one of claims 15 to 22 in which the electroluminescent compound is mixed with the hole transmitting material.
- 5      24. An electroluminescent device as claimed in any one of claims 3 to 23 in which there is a layer of an electron transmitting material between the cathode and the electroluminescent compound layer.
- 10     25. An electroluminescent device as claimed in claim 24 in which the electron transmitting material is a metal quinolate.
26. An electroluminescent device as claimed in claim 25 in which the metal quinolate is an aluminium quinolate or lithium quinolate
- 15     27. An electroluminescent device as claimed in claim 24 in which the electron transmitting material is of formula  $M_x(DBM)_n$  where  $M_x$  is a metal and DBM is dibenzoyl methane and n is the valency of  $M_x$ .
- 20     28. An electroluminescent device as claimed in claim 24 in which the electron transmitting material is a cyano anthracene such as 9,10 dicyano anthracene, a polystyrene sulphonate or a compound of formulae shown in figure 2 or 3 of the drawings.
- 25     29. An electroluminescent device as claimed in any one of claims 24 to 28 in which the electron transmitting material is mixed with the electroluminescent compound.
- 30     30. An electroluminescent device as claimed in any one of the claims 3 to 29 in which the first electrode is a transparent electricity conducting glass electrode.
- 30     31. An electroluminescent device as claimed in any one of the claims 3 to 30 in

- 27 -

which the second electrode is selected from aluminium, calcium, lithium, magnesium and alloys thereof and silver/magnesium alloys.

- 28 -

Abstract

An electroluminescent compound is an organic diiridium acetylacetone complex.

5

10

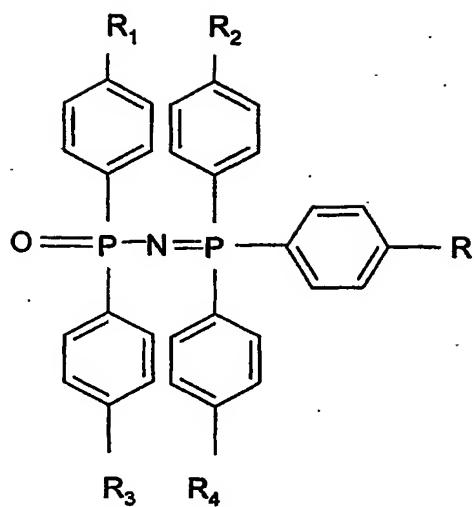


Fig. 1

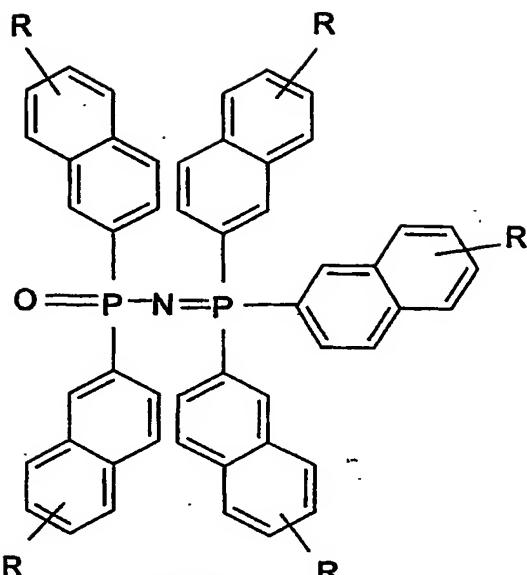


Fig. 2a

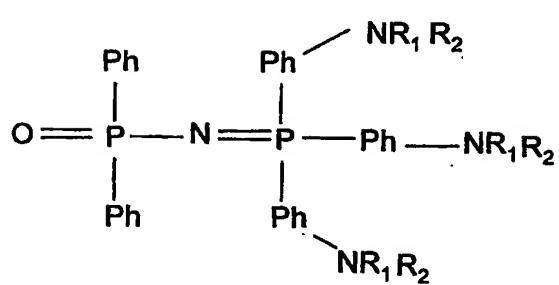


Fig. 2b

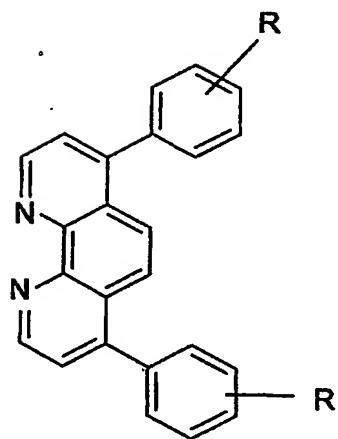


Fig. 3

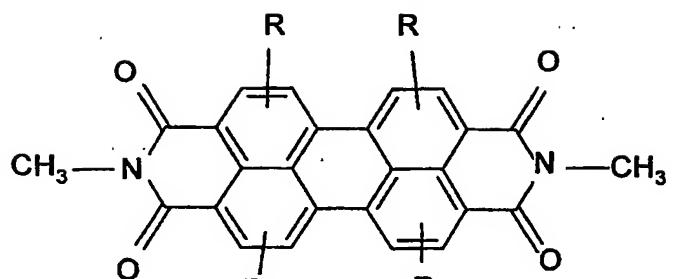


Fig. 4a

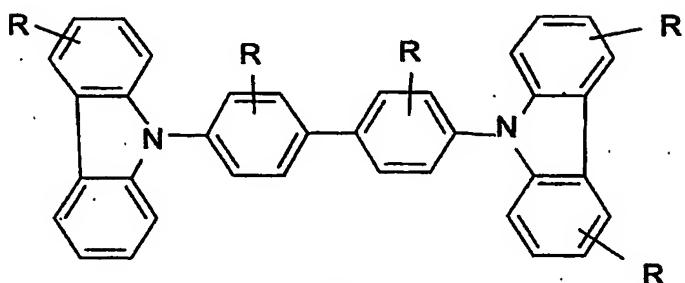


Fig. 4b

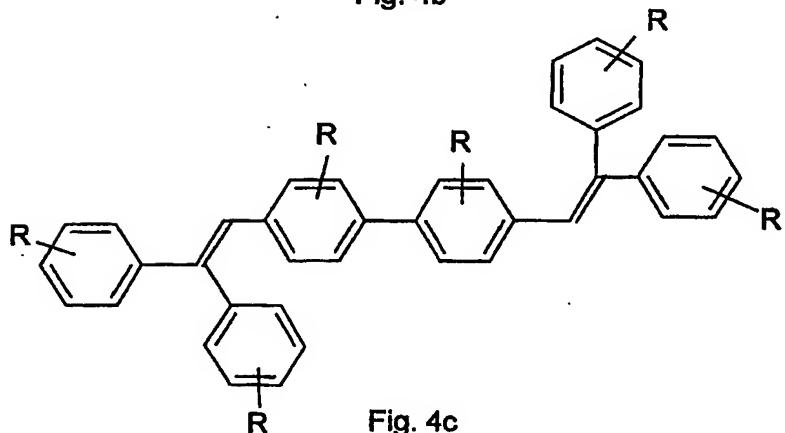


Fig. 4c

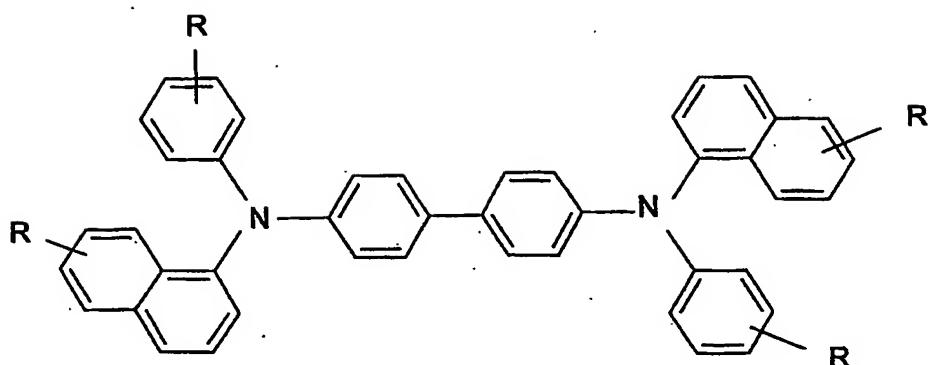


Fig. 4d

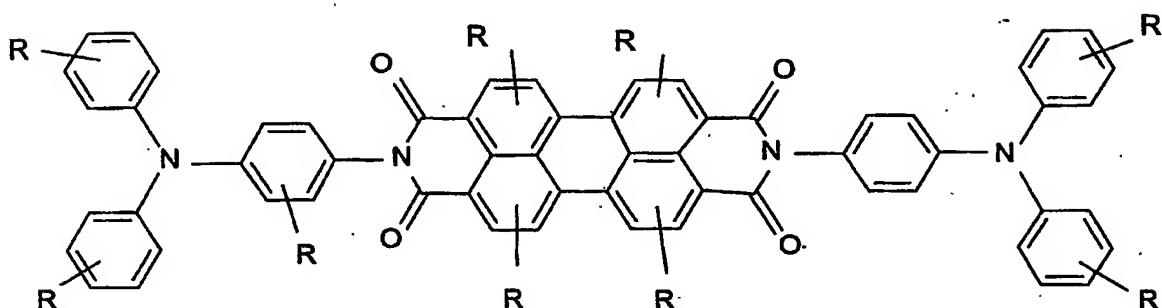


Fig. 4e

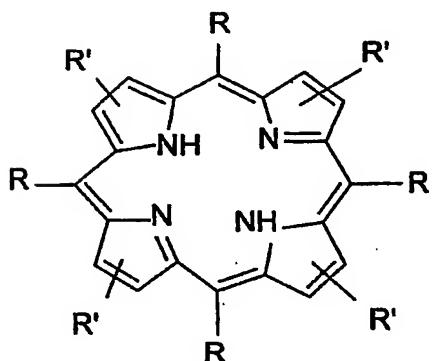


Fig. 4f

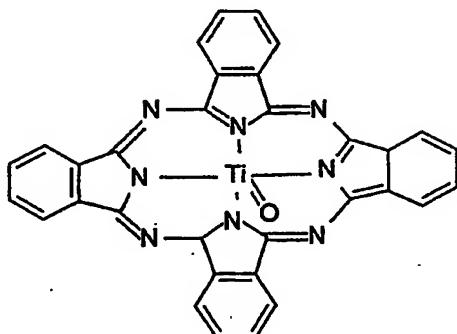


Fig. 4g

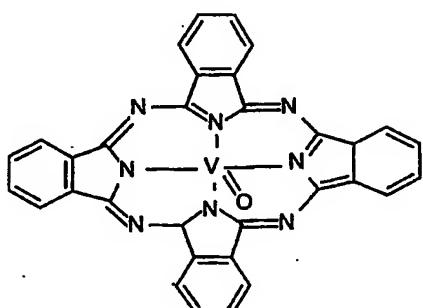


Fig. 4h

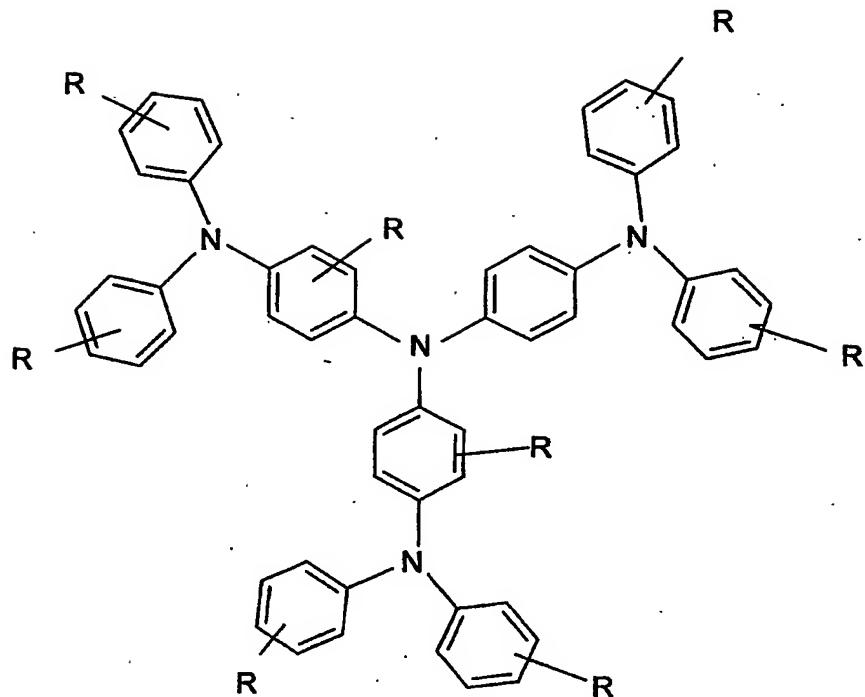


Fig. 4i

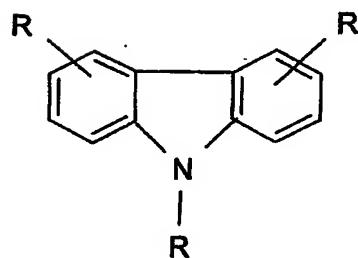


Fig. 4j

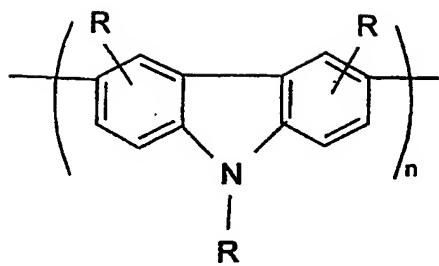


Fig. 4k

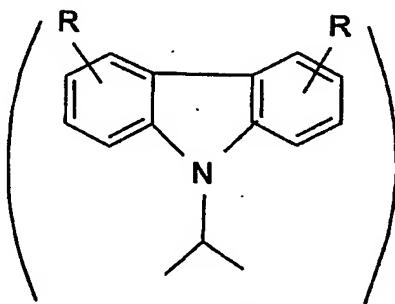


Fig. 4l

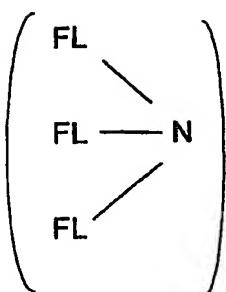


Fig. 5a

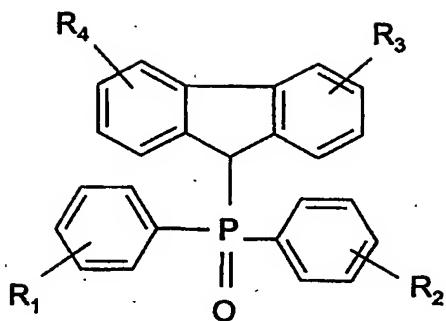


Fig. 5b

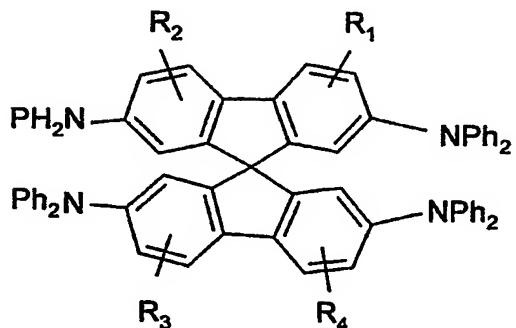
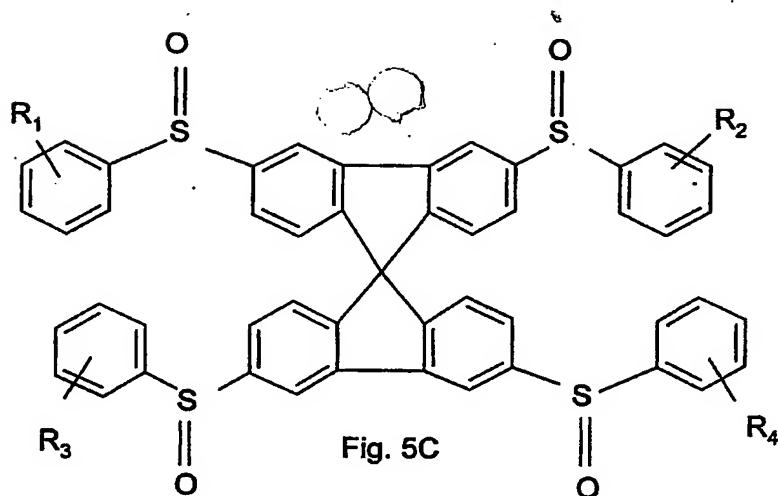


Fig. 5d

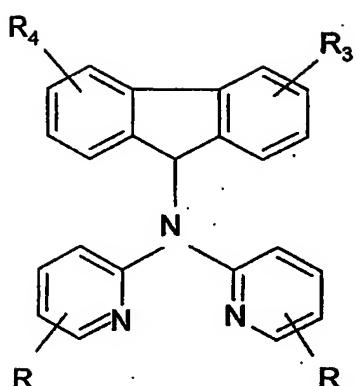


Fig. 5f

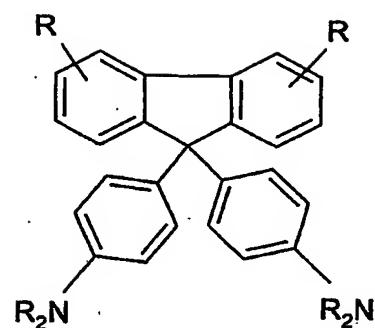


Fig. 5g

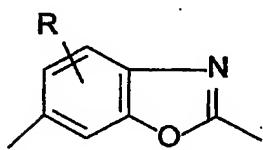


Fig. 6a

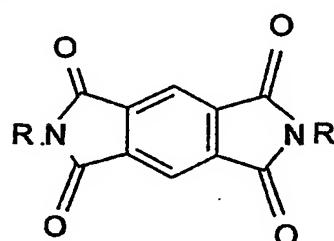


Fig. 6b

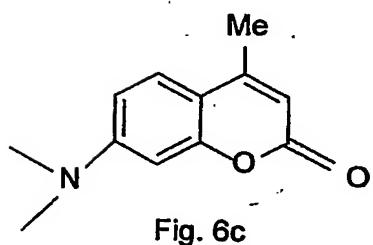


Fig. 6c

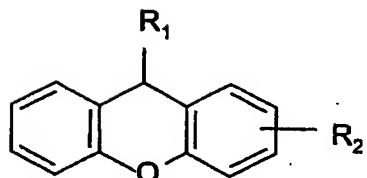


Fig. 6d

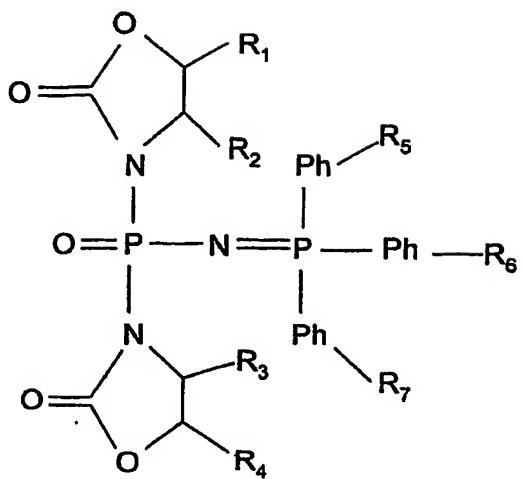


Fig. 6e

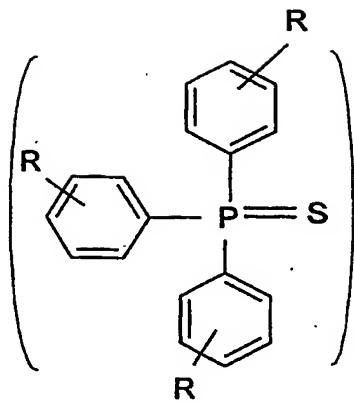


Fig. 7a

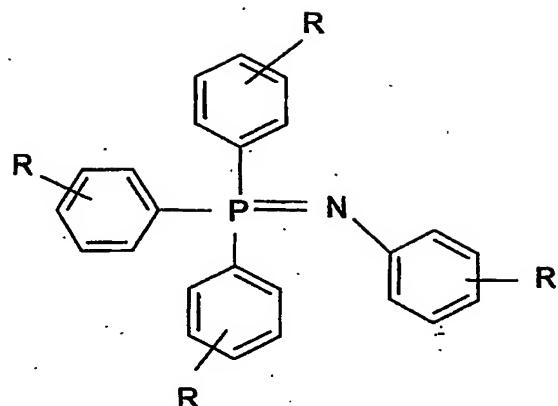


Fig. 7b

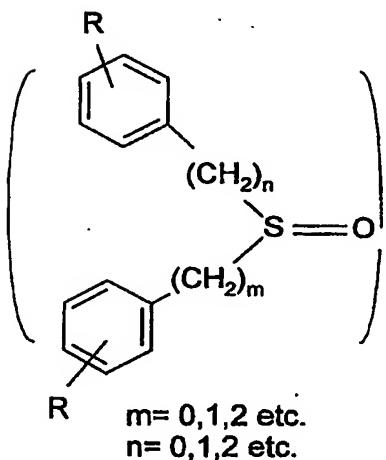


Fig. 7c

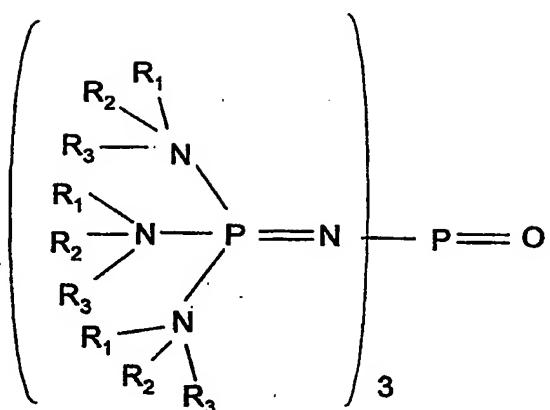


Fig. 7d

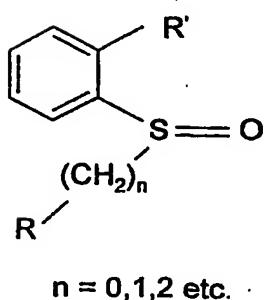


Fig. 7e

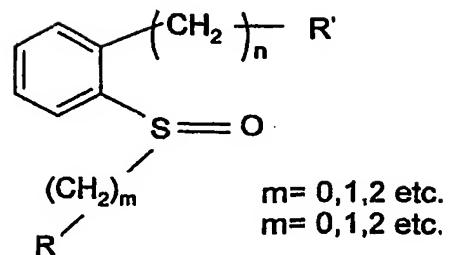


Fig. 7f

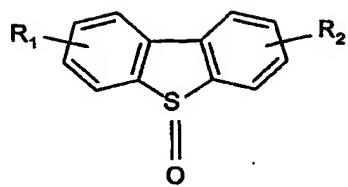


Fig. 8a

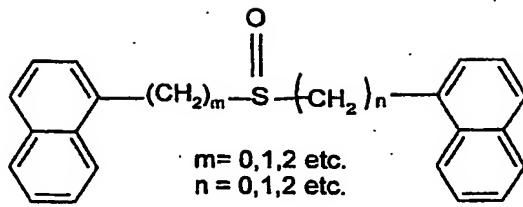


Fig. 8b

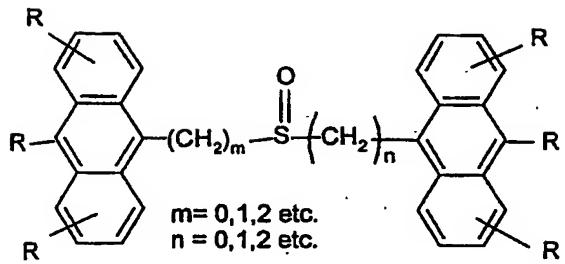


Fig. 8c

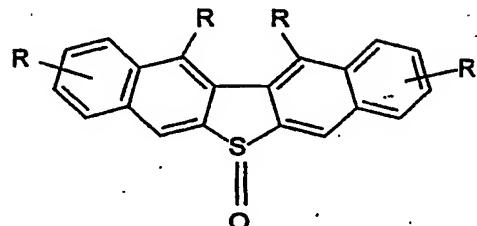


Fig. 8d

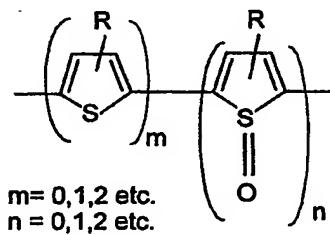


Fig. 8e

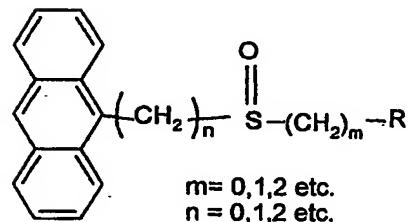


Fig. 8f

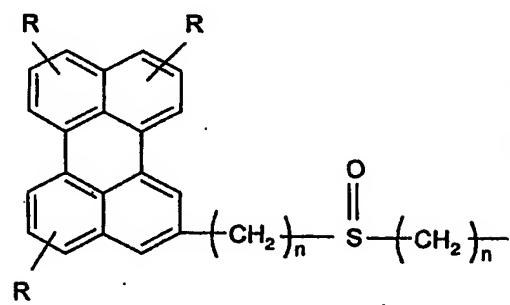
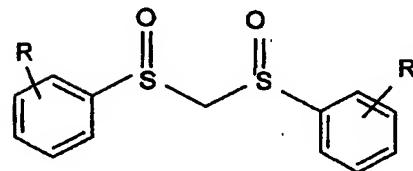
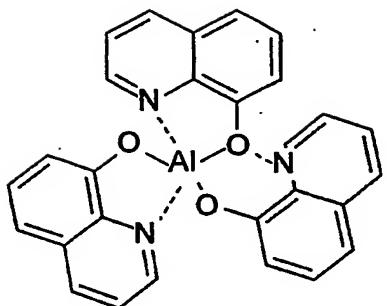


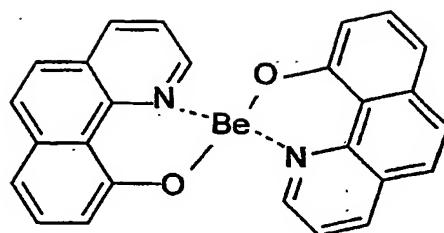
Fig. 8g

Fig. 8g

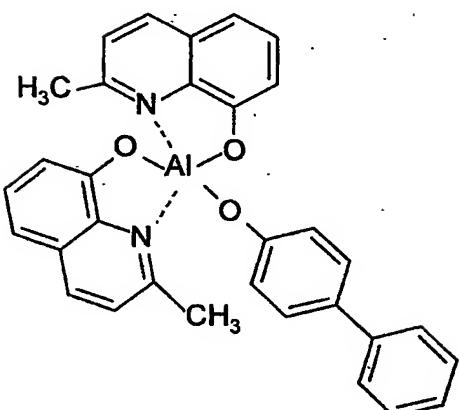




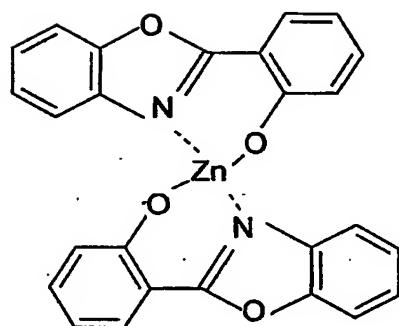
Alq



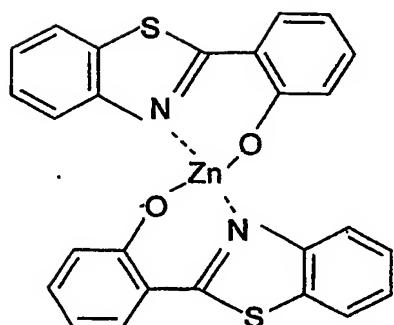
Bebq



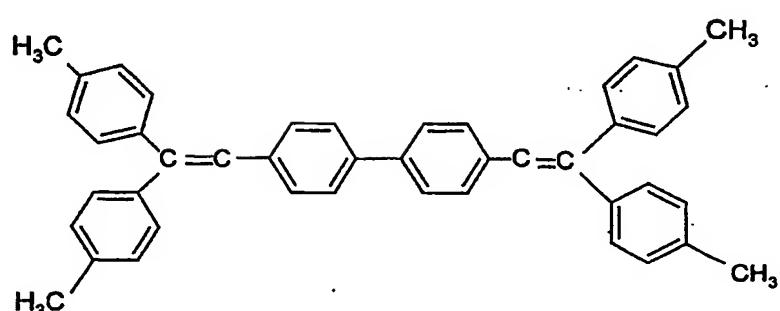
BA1q1



ZnPBO



ZnPBT



DTVb1

Fig. 9

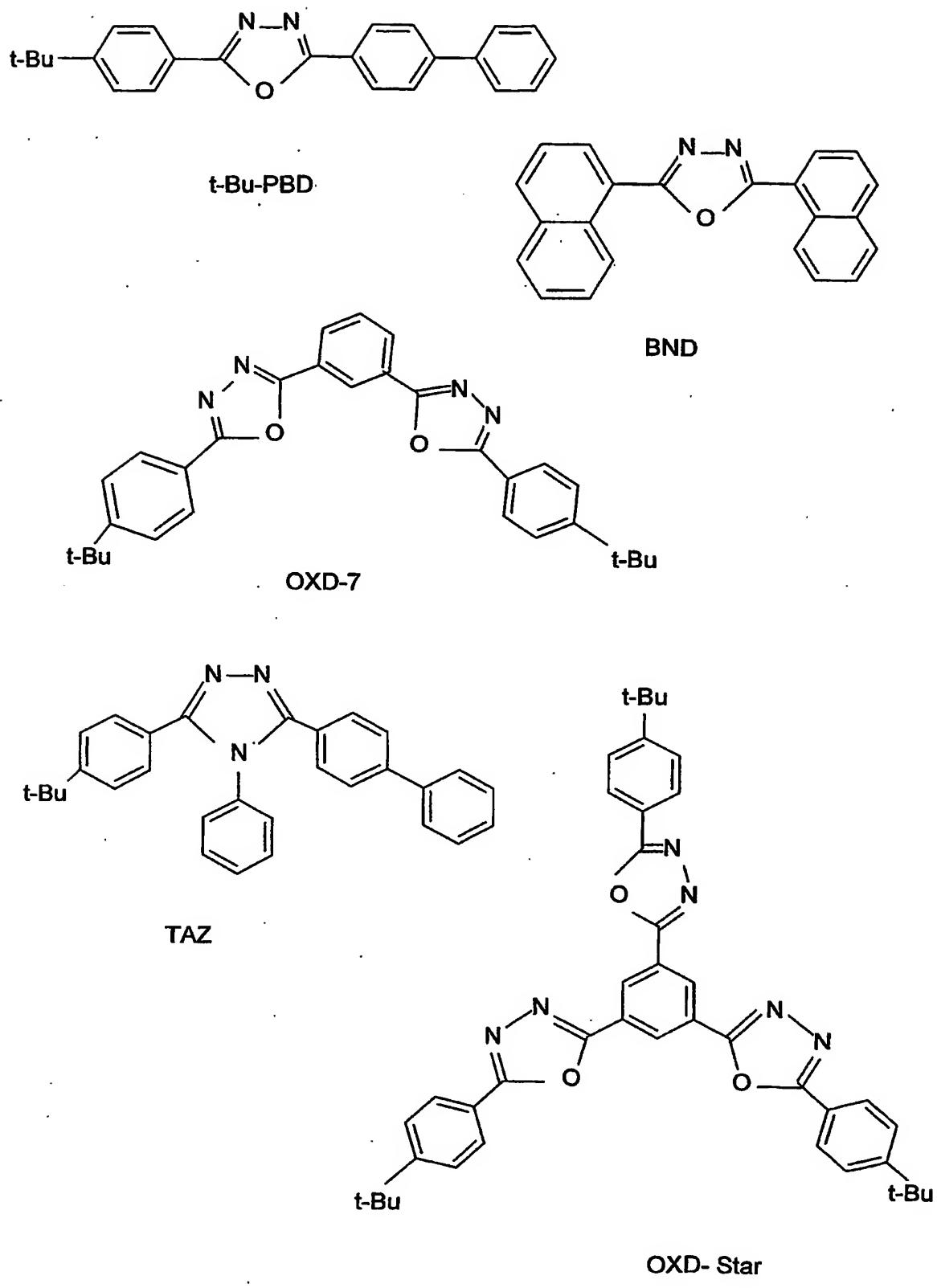
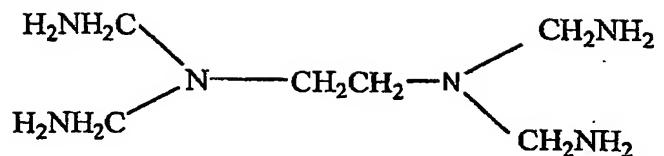
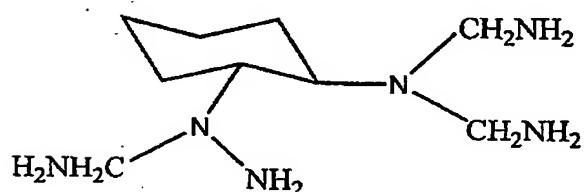


Fig. 10

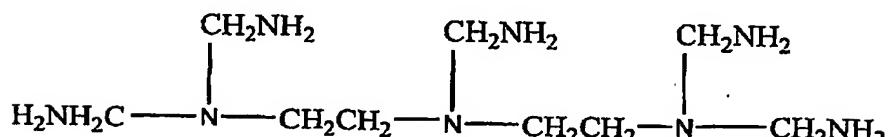
11/20



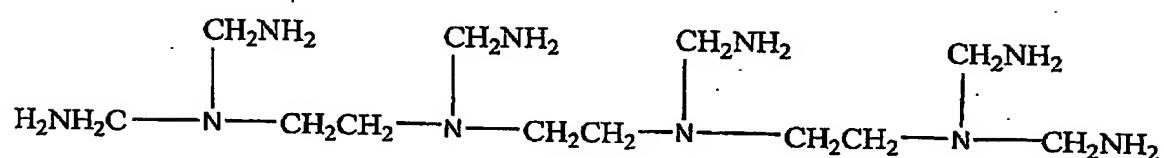
EDTA



DCTA



DTPA



TTHA

Fig. 11

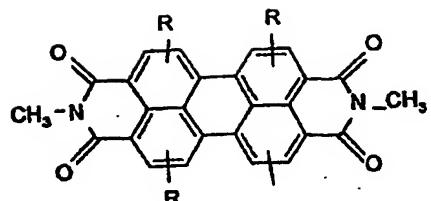


Fig. 12a

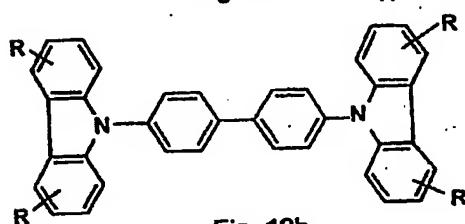


Fig. 12b

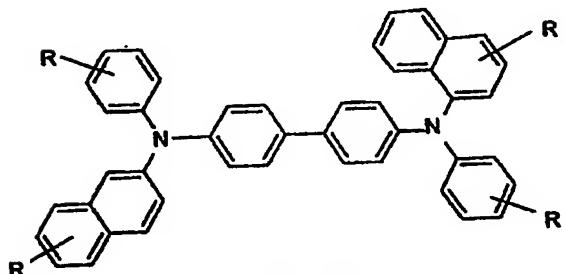


Fig. 12c

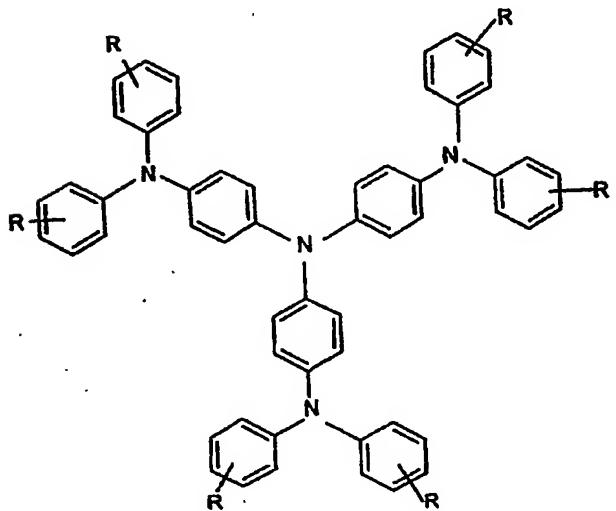


Fig. 12d

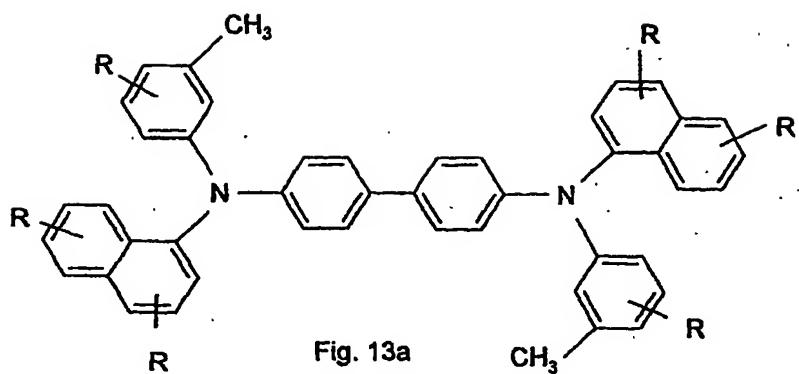


Fig. 13a

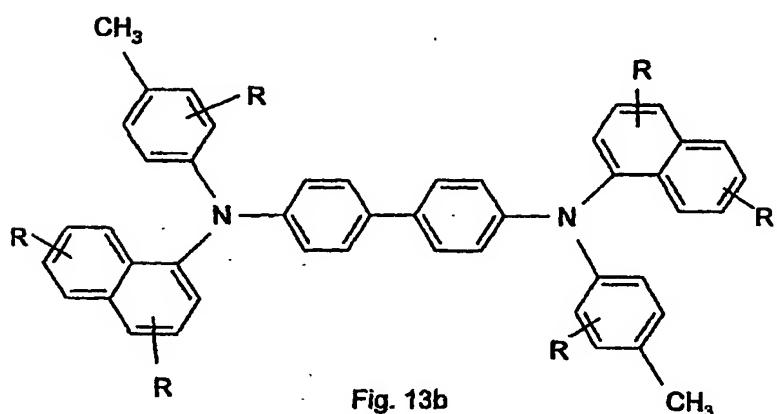


Fig. 13b

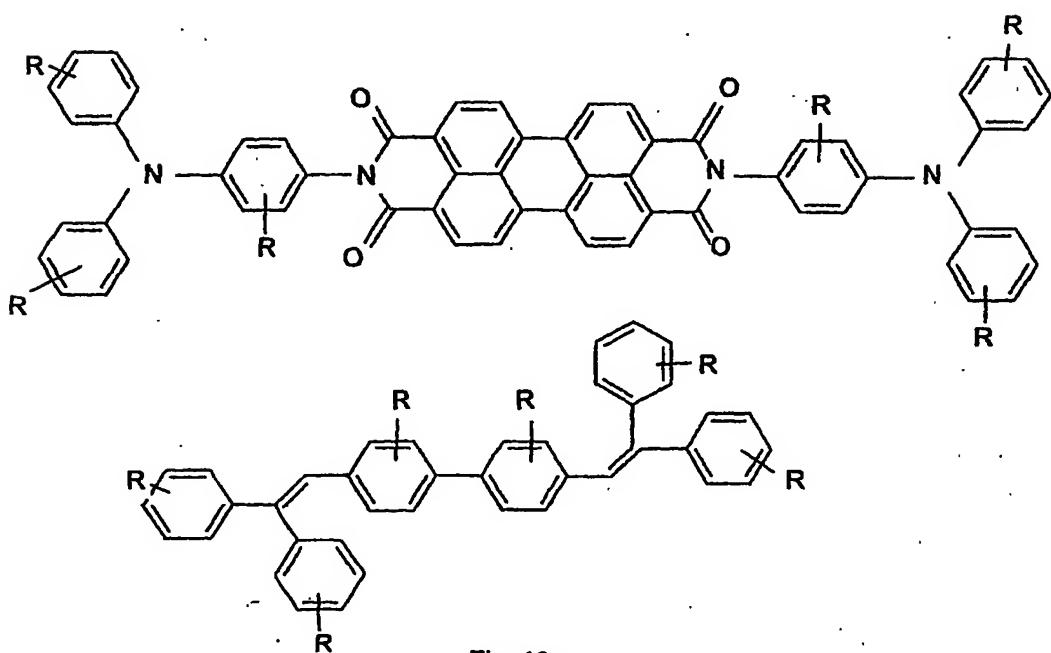


Fig. 13c

14/20

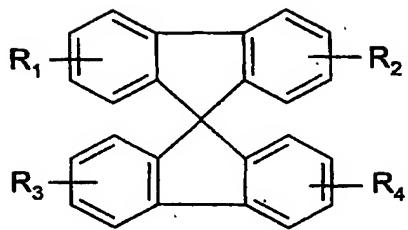


Fig. 14a

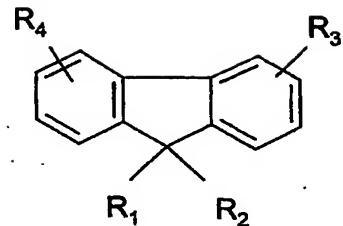
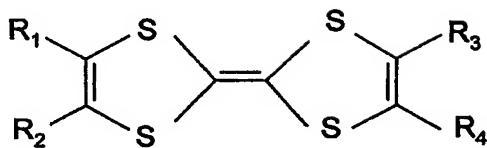


Fig. 14b



or

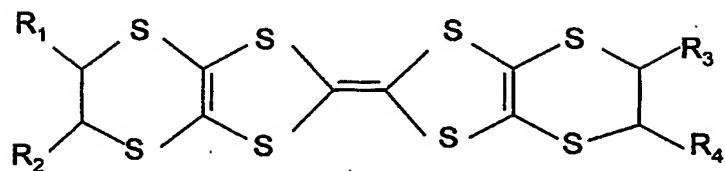


Fig. 14c

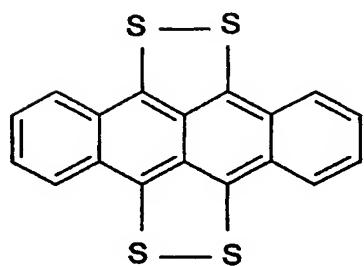


Fig. 14d

15/20

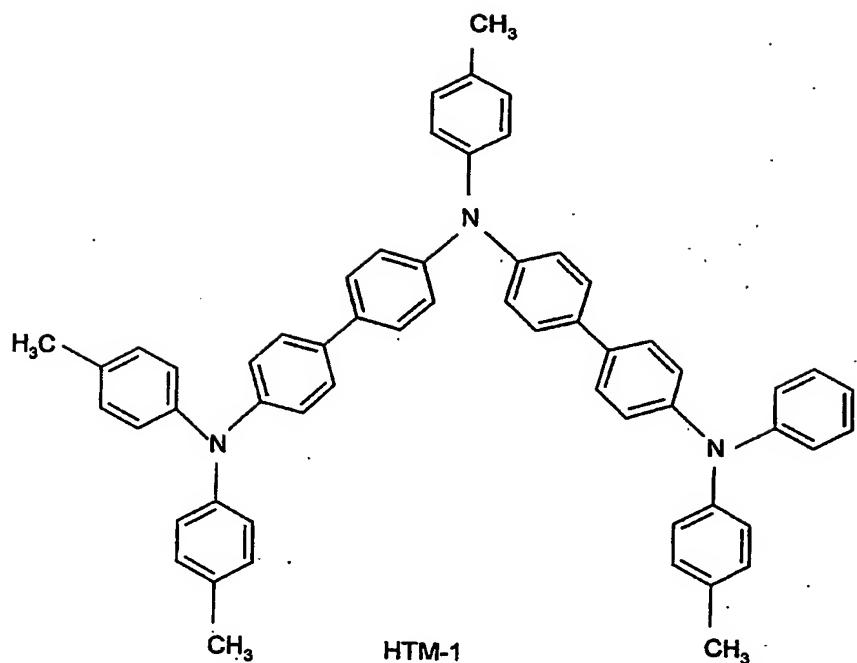


Fig. 15a

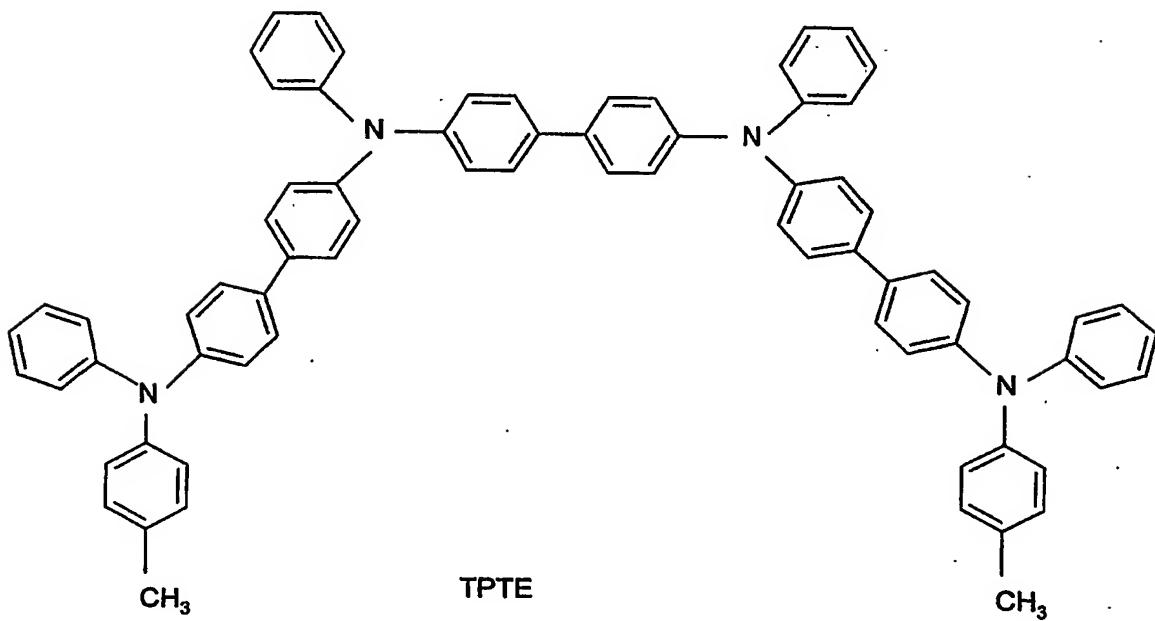
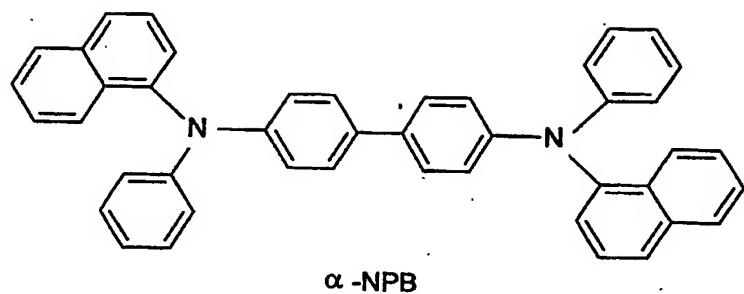
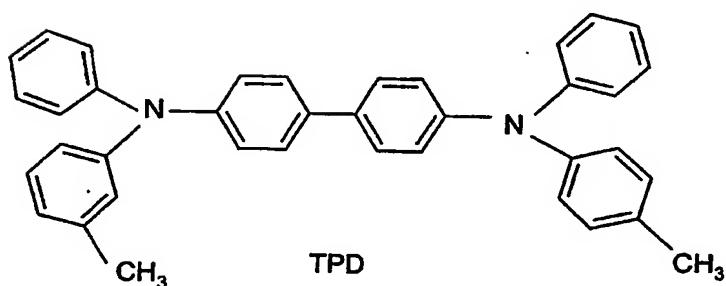


Fig. 15b



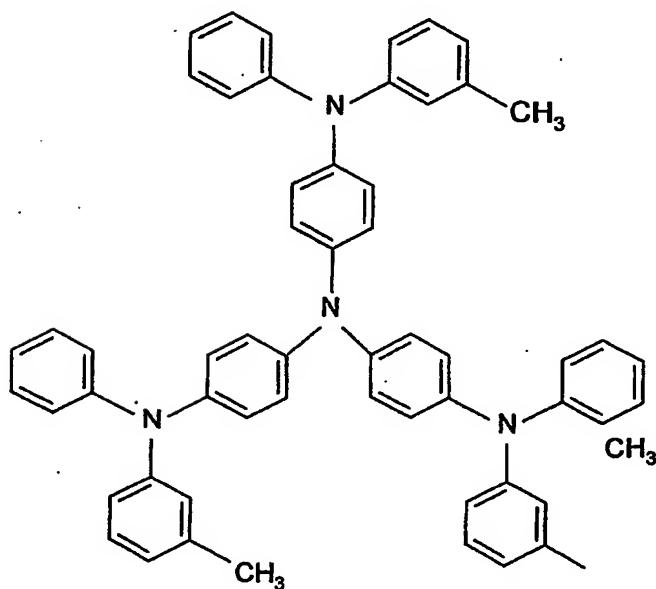
$\alpha$  -NPB

Fig. 16a



TPD

Fig. 16b



mTADATA

Fig. 16c

17/20

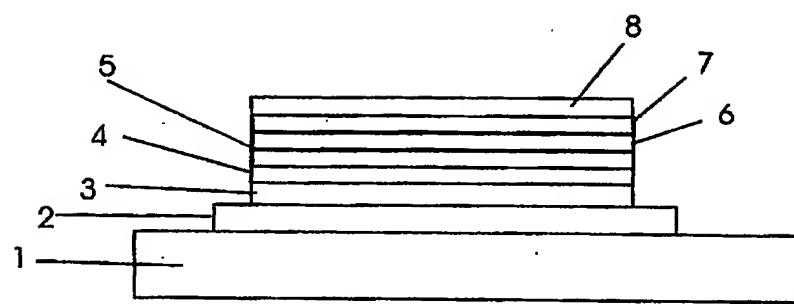


Fig. 17

ITO(100  $\Omega/\text{sq} \text{r})/\text{CuPc} (8 \text{ nm})/\alpha\text{-NPB} (40 \text{ nm})/\text{CBP+Ir}_2(\text{diacac})_2(\text{dpp})_2 (20 \text{ nm})/\text{BCP} (6 \text{ nm})/\text{Al}$

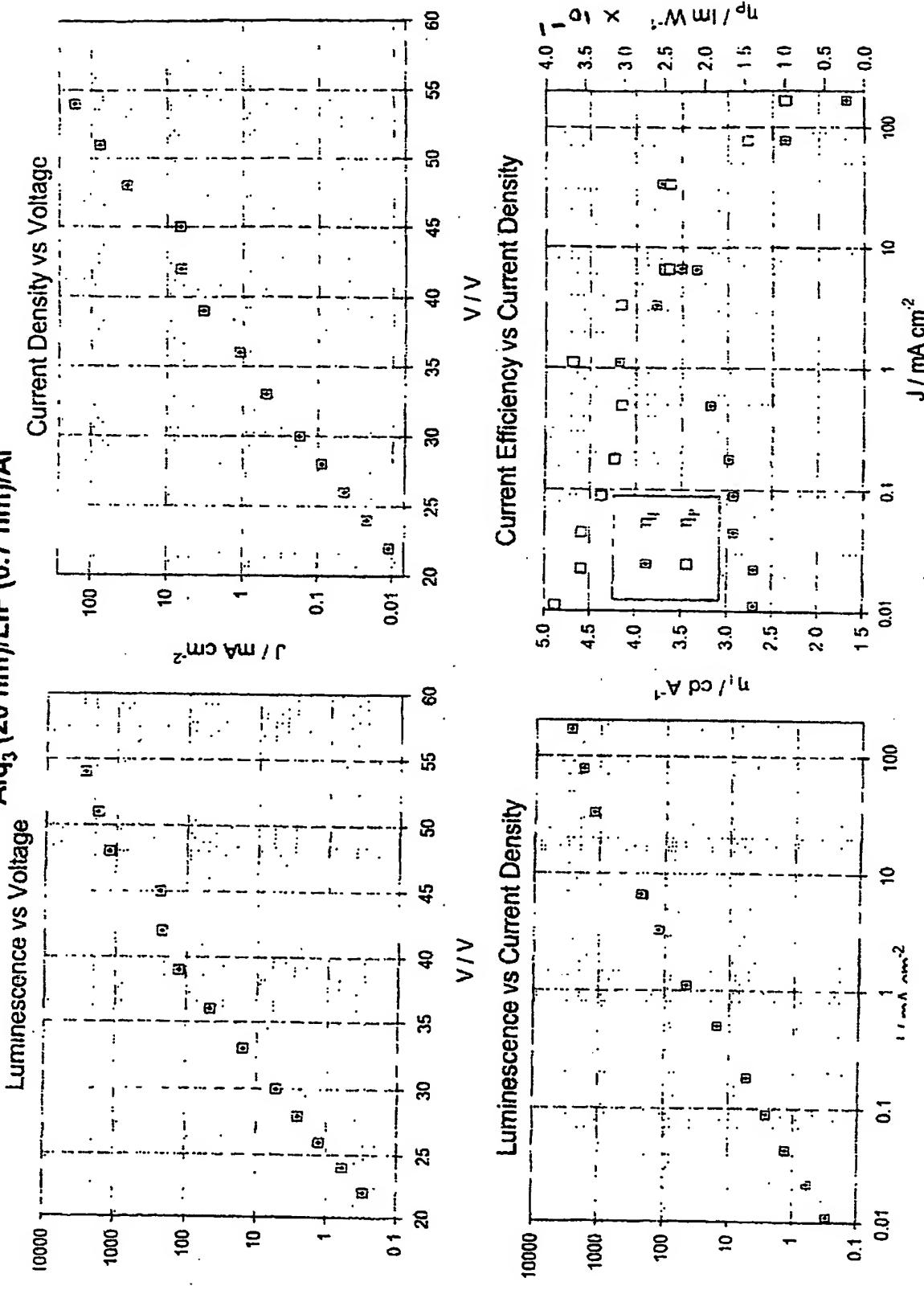
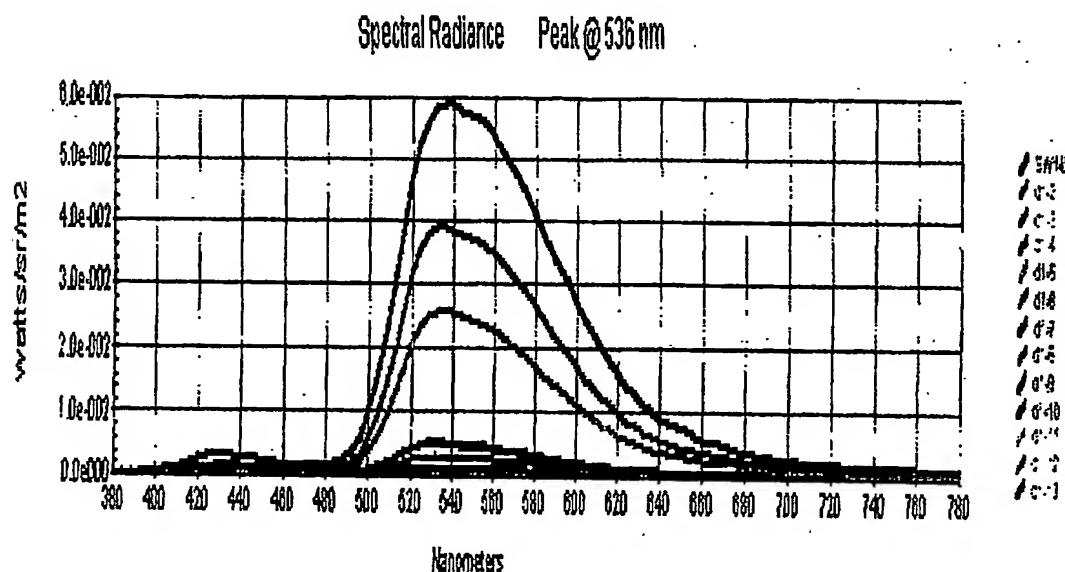


Fig. 18

Device ID: F2I

**Device Configuration:**

**ITO (100  $\Omega/\square$ )/CuPc (8 nm)/ $\alpha$ -NPB (40 nm)/CBP+Ir<sub>2</sub>(diacac)(dpp)<sub>2</sub> (12%) (20 nm)/BCP (6 nm)/Alq<sub>3</sub> (20 nm)/LiF (0.7 nm)/Al**



Voltage / V	Colour Co-ordinates	
	X	y
22	0.35	0.57
24	0.36	0.59
26	0.36	0.59
28	0.36	0.59
30	0.36	0.59
33	0.36	0.59
36	0.37	0.59
39	0.37	0.59
42	0.37	0.59
45	0.37	0.59
48	0.38	0.58
51	0.38	0.57
54	0.38	0.56

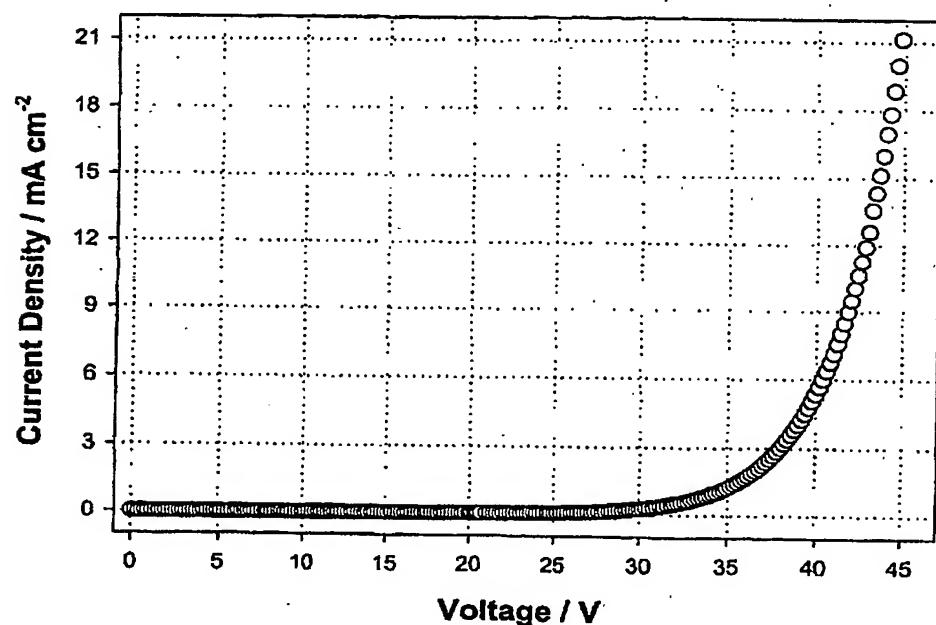
Fig. 19

20/20

**Device Configuration:**

**ITO (100  $\Omega/\square$ )/CuPc (8 nm)/ $\alpha$ -NPB (40 nm)/CBP+Ir<sub>2</sub>(diacac)(dpp)<sub>2</sub> (12%) (20 nm)/BCP (6 nm)/Alq<sub>3</sub> (20 nm)/LiF (0.7 nm)/Al**

**J vs V Characteristics**



**Fig. 20**

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.